

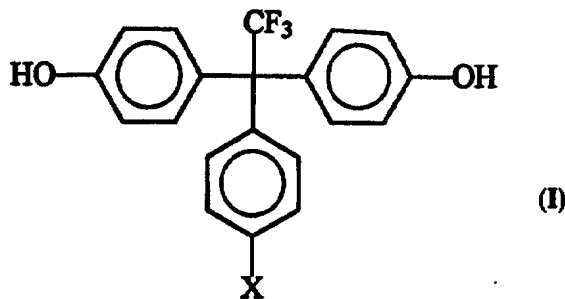
PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : G03F 7/022, 7/004		A1	(11) International Publication Number: WO 96/12988
			(43) International Publication Date: 2 May 1996 (02.05.96)
(21) International Application Number: PCT/US95/12719		(81) Designated States: CN, JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 12 October 1995 (12.10.95)			
(30) Priority Data: 08/327,758 24 October 1994 (24.10.94) US 08/446,261 22 May 1995 (22.05.95) US		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(71) Applicant: HOECHST CELANESE CORPORATION [US/US]; Route 202-206 North, Somerville, NJ 08876 (US).			
(72) Inventors: RAHMAN, M., Dalil; 62 Concord Ridge Road, Flemington, NJ 08822 (US). AUBIN, Daniel, P.; 202 Condgon Road, P.O. Box 276, Voluntown, CT 06384 (US).			
(74) Agents: SAYKO, Andrew, F., Jr. et al.; Hoechst Celanese Corporation, 70 Meister Avenue, Somerville, NJ 08876 (US).			

(54) Title: POSITIVE PHOTOSENSITIVE COMPOSITION**(57) Abstract**

A photosensitizer comprising a diazo ester of structure (I) wherein: X = Cl, Br, I, OH, OR, COOR, COOAr(OH)_n, COAr(OH)_n, COR, R, Ar(OH)_n; R = C₁-C₈ alkyl, n = 0 to 5, Ar = phenyl, as the backbone, where at least one of the hydroxy groups on phenyl ring has been esterified with diazo-sulfonyl chloride comprising 60 to 100 mole % 2,1,4 or 2,1,5-diazo sulfonyl chloride, or a mixture thereof, and a photoresist comprising an admixture of the photosensitizer, which is present in the photoresist composition in an amount sufficient to uniformly photosensitize the photoresist composition; a water insoluble, aqueous alkali soluble novolak resin, the novolak resin being present in the photoresist composition in an amount sufficient to form a substantially uniform photoresist composition and a suitable solvent.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

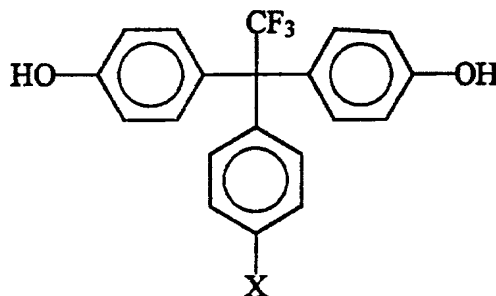
AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LV	Latvia	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon				

DESCRIPTION

POSITIVE PHOTSENSITIVE COMPOSITION

Filed of the Invention

5 The present invention relates to positive photoresist compositions especially sensitive in the broad band range of the spectrum (365-436 nm), based on a diazonaphthoquinone sensitizer using a compound of the following structure as a backbone, a novolak resin and a solvent.



X = Cl, Br, I, OH, OR, COOR, COOAr(OH)_n, COAr(OH)_n, COR, R, Ar(OH)_n

R = C₁-C₈ alkyl, n = 0 to 5, Ar = Phenyl

10 Description of Related Art

Photoresists are materials which change their solubility in a developer solution after the photoresist has been exposed to actinic radiation, such as to ultra violet radiation. Photoresist compositions comprise a photosensitive compound (sometimes called a photosensitizer), a film forming polymeric resin and a solvent. There are other
15 types of compositions possible, such as a photosensitizer composition dissolved in an appropriate solvent. The photoresist composition is applied to a substrate which is to be patterned and the solvent is then removed, as with heat, leaving the photoresist as a thin film covering the substrate. As a consequence of the exposure to radiation of the photoresist, a different solubility rate results between the exposed and unexposed
20 (masked over) portions of the resist film which yields a surface relief pattern after development. Those photoresists which become more soluble in a developer solution in the exposed regions are referred to as "positive" photoresists. Those which become less soluble in the exposed regions are referred to as "negative" photoresists. The

- 2 -

present invention deals with a class of those compounds suitable for use in positive photoresist compositions.

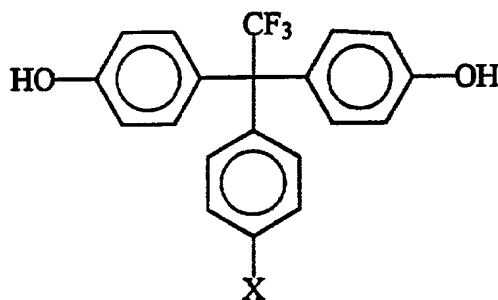
Positive photoresists may comprise an aqueous alkali soluble resin, such as a novolak resin or a poly(hydroxystyrene), and a photosensitizer. The resin and
5 sensitizers are applied, such as by spin coating, spray coating, or other suitable means, from an organic solvent or solvent mixture onto a substrate, such as a silicon wafer or a chrome-plated glass plate. The developer used to process the positive photoresists are aqueous alkaline solutions, such as sodium metasilicate, potassium hydroxide, tetramethyl ammonium hydroxide and ammonium hydroxide. The developer removes
10 the areas of the coated photoresist film that have been exposed to light or other form of irradiation so as to produce a relief pattern in the photoresist film.

The application of a photosensitive film to various substrates is an essential step in the fabrication of integrated circuits. The substrates are generally silicon wafers which may have a thin oxide coating or other coating such as silicon nitride or
15 aluminum. The photosensitive film is used to pattern the substrate in a series of steps including exposure (through a mask pattern), development to yield a relief pattern in the resist layer and a substrate etch step to transfer that pattern into the substrate material. It is essential that the mask pattern be accurately reproduced in the substrate etch pattern. To achieve this high degree of accuracy, the mask pattern must be well
20 resolved by the photoresist layer. Conventional photoresists may employ novolak resins as the alkali soluble, film forming polymer.

Background of the Invention

The present invention relates to radiation sensitive positive working photoresist compositions and particularly to compositions containing novolak resins together with
25 a photosensitizer which is a diazo sulfonyl diester produced by reacting 2,1,4 or 2,1,5 diazo sulfonyl chloride with the following structure as a backbone:

- 3 -



X = Cl, Br, I, OH, OR, COOR, COOAr(OH)_n, COAr(OH)_n, COR, R, Ar(OH)_n

R = C₁-C₈ alkyl, n = 0 to 5, Ar = Phenyl

It is known to the skilled artisan to produce positive photoresist compositions such as those described in United States Patent Nos. 3,666,473; 4,115,128 and 4,173,470. These include water insoluble, aqueous alkali-soluble phenol-formaldehyde novolak resins together with light-sensitive materials, usually a substituted naphthoquinone diazide compound. The resins and sensitizers are dissolved in an organic solvent or mixture of solvents and are applied as a thin film or coating to a substrate suitable for the particular application desired.

The novolak resin component of these photoresist formulations is soluble in aqueous alkaline solutions, but the sensitizer is not soluble prior to exposure. Upon imagewise exposure of portions of the coated substrate to actinic radiation, the sensitizer is rendered alkali soluble and the exposed areas of the coating become more soluble than the unexposed areas. This difference in solubility rates causes the exposed areas of the photoresist coating to be dissolved when the substrate is immersed in or otherwise contacted with an alkaline developing solution, while the unexposed areas are largely unaffected, thus producing a positive relief pattern on the substrate. The exposed and developed substrate is usually thereafter subjected to an etching process. The photoresist coating protects the coated areas of the substrate from the etchant and the etchant is only able to etch the uncoated areas of the substrate, which correspond to the areas that were exposed to actinic radiation. Thus, an etched pattern can be created on the substrate which corresponds to the pattern of the mask, stencil, template, etc.,

that was used to create selective exposure patterns on the coated substrate prior to development. The relief pattern of photoresist on a substrate produced by this method is useful for various applications including the manufacture of miniaturized integrated circuits.

5 The characteristics of the photoresist compositions, which are important in commercial practice, include its photospeed, contrast, resolution (edge acuity), thermal stability of the image during processing, processing latitude, line width control, clean development and unexposed film loss.

10 Photoresist contrast is the slope of the linear portion of the curve resulting from the plot of the log of exposure energy vs. normalized film thickness remaining under fixed development conditions. In use, development of an exposed resist coated substrate is continued until the coating on the exposed area is substantially completely dissolved away. Resolution refers to the capability of a resist system to reproduce the smallest equally spaced line pairs and intervening spaces of a mask which is utilized
15 during exposure with a high degree of image edge acuity in the developed exposed spaces. In the manufacture of miniaturized electronic components, a photoresist is required to provide a high degree of resolution for very small line and space widths usually on the order of one micron or less. This capability to reproduce very small dimensions, is extremely important in the production of large scale integrated circuits
20 on silicon chips and similar components. Circuit density on such a chip can only be increased, assuming photolithography techniques are utilized, by increasing the resolution capabilities of the resist. Although negative photoresists, wherein the exposed areas of resist coating become insoluble and the unexposed areas are dissolved away by the developer, have been extensively used for this purpose by the
25 semiconductor industry, positive photoresists have inherently higher resolution and are utilized as replacements for the negative resists.

 In photoresist technology, it has normally been desired to increase resist contrast. High contrast positive working resists produce developed images which exhibit high edge acuity, when exposure is performed on typical equipment such as
30 steppers and projection aligners. In most lithographic semiconductor applications, the high edge acuity of developed images is of great importance since it allows for small

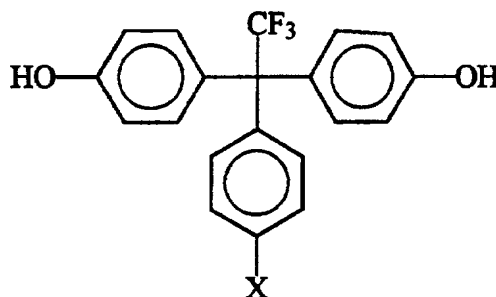
- 5 -

variations of line width over the wafer's topography. Therefore, it permits good control of etching during anisotropic plasma-etching and is typically associated with good processing latitude.

Summary of the Invention

5 The invention provides a new photosensitizer and new positive photoresist compositions containing this photosensitizer. Such photoresist compositions have good photospeed, high contrast, good resolution, good thermal stability of the image during processing, wide processing latitude, good line width control, clean development and low unexposed film loss.

10 The photosensitive compound of the present invention comprises: a diazo sulfonyl ester of a compound having the following structure as a backbone:



X = Cl, Br, I, OH, OR, COOR, COOAr(OH)_n, COAr(OH)_n, COR, R, Ar(OH)_n

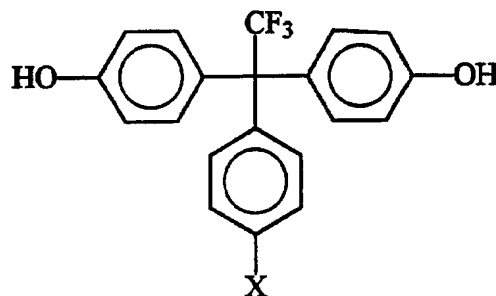
R = C₁-C₈ alkyl, n = 0 to 5, Ar = Phenyl

15 wherein the diazo ester is a compound wherein at least one hydroxy group on the Phenylring has been esterified with a diazosulfonyl chloride. On average, from about 60 mole percent to about 100 mole percent of the hydroxy groups of the above structure have been esterified by the diazosulfonyl chloride. The diazo ester moiety is from about 60 to 100 mole percent 2,1,4-diazo sulfonyl chloride or 2,1,5-diazo sulfonyl chloride, or a mixture thereof. Preferably the diazo ester distribution ranges from 75 to 20 100 mole percent and most preferably from about 85 to 95 mole percent.

 The invention also provides a method for producing a positive photoresist composition, which comprises providing an admixture of:

- 6 -

- (a) a photosensitive component containing a diazo sulfonyl ester of a compound having the following structure as a backbone:



X = Cl, Br, I, OH, OR, COOR, COOAr(OH)_n, COAr(OH)_n, COR, R, Ar(OH)_n

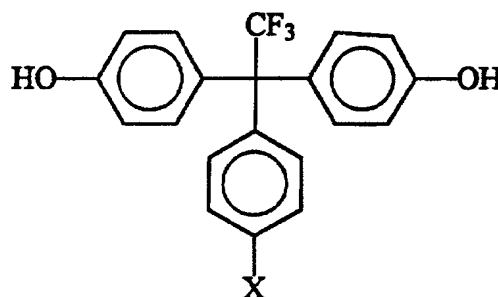
R = C₁-C₈ alkyl, n = 0 to 5, Ar = Phenyl

- 5 wherein the diazo ester is a compound wherein at least one hydroxy group on the Phenylring has been esterified with a diazosulfonyl chloride; on average, from about 60 mole percent to about 100 mole percent of the hydroxy groups of the above structure type molecule have been esterified by one diazosulfonyl chloride, the photosensitive component being present in the photoresist composition in an amount
- 10 sufficient to uniformly photosensitize the photoresist composition; the diazo moiety ester is from 60 to about 100 mole percent 2,1,4 or 2,1,5 diazo ester or mixture thereof; preferably the diazo ester distribution range from 75 to 100 mole percent and most preferably from about 85
- 15 to 95 mole percent;
- (b) a water insoluble, aqueous alkali soluble novolak resin; the novolak resin being present in the photoresist composition in an amount sufficient to form a substantially uniform photoresist composition; and
- (c) a suitable solvent, preferably propylene glycol methyl ether acetate
- 20 (PGMEA), 2-heptanone, ethyl lactate, ethyl 3-ethoxy propionate (EEP) or a mixture thereof.

- 7 -

The positive photoresist composition comprises an admixture of:

- (a) a photosensitive component containing a diazo sulfonyl ester of a compound having the following structure as a backbone:



X = Cl, Br, I, OH, OR, COOR, COOAr(OH)_n, COAr(OH)_n, COR, R, Ar(OH)_n

5 R = C₁-C₈ alkyl, n = 0 to 5, Ar = Phenyl

the diazo ester is a compound wherein at least one hydroxy group on the phenylring has been esterified with a diazosulfonyl chloride; on average, from about 60 mole percent to about 100 mole percent of the hydroxy groups of the above structure type molecule have been esterified by the diazosulfonyl chloride; the photosensitive component being present in the photoresist composition in an amount sufficient to uniformly photosensitize the photoresist composition; the diazo ester moiety is from about 60 to 100 mole percent of 2,1,4-diazo sulfonyl chloride or 2,1,5-diazo sulfonyl chloride, or a mixture thereof; preferably the diazo ester distribution range from 75 to 100 mole percent and most preferably from about 85 to 95 mole percent;

- (b) a water insoluble, aqueous alkali soluble novolak resin; the novolak resin being present in the photoresist composition in an amount sufficient to form a substantially uniform photoresist composition; and
- (c) a suitable solvent, such as propylene glycol methyl ether acetate (PGMEA), ethyl lactate, ethyl 3-ethoxy propionate (EEP) or a mixture of two or more thereof;

- 8 -

- (d) heat treating the coated substrate until substantially all of the solvent composition is removed;
- (e) imagewise exposing the photosensitive composition to actinic radiation; and
- 5 (f) removing the image-wise exposed areas of the composition with an aqueous alkaline developer (optionally, one may perform a baking of the substrate either immediately before or after the removing step).

The coating solvents may be present in the overall composition in an amount of up to about 95% by weight of the solids in the composition. Solvents, of course are
10 substantially removed after coating of the photoresist solution on a substrate and drying. Non-ionic surfactants that may be used include, for example, nonylphenoxy poly(ethyleneoxy) ethanol; octylphenoxy ethanol at up to 10% weight levels, based on the combined weight of novolak and sensitizer.

The prepared resist solution, can be applied to a substrate by any conventional
15 method used in the photoresist art, including dipping, spraying, whirling and spin coating. When spin coating, for example, the resist solution can be adjusted with respect to the percentage of solids content in order to provide coating of the desired thickness given the type of spinning equipment utilized and the amount of time allowed for the spinning process. Suitable substrates include silicon, aluminum, polymeric
20 resins, silicon dioxide, doped silicon dioxide, silicon nitride, tantalum, copper, polysilicon, ceramics, aluminum/copper mixtures; gallium arsenide and other such Group III/V compounds. The photoresist coatings produced by the above described procedure are particularly suitable for application to thermally grown silicon/silicon dioxide-coated wafers such as are utilized in the production of microprocessors and
25 other miniaturized integrated circuit components. An aluminum/aluminum oxide wafer can be used as well. The substrate may also comprise various polymeric resins especially transparent polymers such as polyesters. The substrate may have an adhesion promoted layer of a suitable composition such as one containing hexa-alkyl disilazane.

30 The resist composition solution is then coated onto the substrate, and the substrate is heat treated at from about 80°C to about 110°C for from about 30 seconds

to about 180 seconds on a hot plate or for from about 15 to about 40 minutes in a convection oven. This temperature treatment is selected in order to reduce the concentration of residual solvents in the photoresist while not causing substantial thermal degradation of the photosensitizer. In general one desires to minimize the concentration of solvents and thus this first temperature treatment is conducted until substantially all of the solvents have evaporated and a thin coating of photoresist composition, on the order of a micron in thickness, remains on the substrate. In a preferred embodiment the heat treatment is conducted at from about 85°C to about 95°C. The treatment is conducted until the rate of change of solvent removal becomes relatively insignificant. The temperature and time selection depends on the resist properties desired by the user as well as equipment used and commercially desired coating times. The coating substrate can then be exposed to actinic radiation, especially ultraviolet radiation, at a wavelength of from about 300 nm to about 450 nm (preferably at about 365 nm), x-ray, electron beam, ion beam or laser radiation, in any desired pattern, produced by use of suitable masks, negatives, stencils, templates, etc.

The resist is then optionally subjected to a post exposure second baking or heat treatment, either before or after development. The heating temperatures may range from about 90°C to about 150°C, more preferably from about 110°C to about 150°C. The heating may be conducted for from about 10 seconds to about 30 minutes, more preferably from about 45 seconds to about 90 seconds on a hot plate or about 10 to about 30 minutes by convection oven.

The exposed resist-coated substrates are developed to remove the imagewise exposed, non-image areas by spray developing using an alkaline developing solution. The solution is preferably agitated, for example, by nitrogen burst agitation. The substrates are allowed to remain in the developer until all, or substantially all, of the resist coating has dissolved from the exposed areas. Developers may include aqueous solutions of ammonium or alkali metal hydroxides. One preferred hydroxide is tetramethyl ammonium hydroxide (TMAH). A suitable developer is AZ® Developer available commercially from the AZ Photoresist Products group of Hoechst Celanese Corporation, Somerville, New Jersey. After removal of the coated wafers from the developing solution, one may conduct an optional post-development heat treatment or

bake to increase the coating's adhesion and chemical resistance to etching solutions and other substances. The post-development heat treatment can comprise the oven baking of the coating and substrate below the coating's softening point. In industrial applications, particularly in the manufacture of microcircuitry units on silicon/silicon dioxide-type substrates, the developed substrates may be treated with a buffered, hydrofluoric acid base etching solution. The resist compositions of the present invention are resistant to acid-base etching solutions and provide effective protection for the unexposed resist-coating areas of the substrate.

The following specific examples will provide detailed illustrations of the methods of producing and utilizing the compositions of the present invention. These examples are not intended to limit or restrict the scope of the invention in any way and should not be construed as providing conditions, parameters or values which must be utilized exclusively in order to practice the present invention.

EXAMPLE 1

Synthesis of 2,1,5-and 2,1,4-Diazo Ester of 1,1-Bis(4-hydroxyphenyl)-1-(4-bromophenyl)-2,2,2,-trifluoro ethane

Into a 200 ml., four necked flask equipped with a thermometer, stirring shaft and dropping funnel were added 5.0 grams (.01182 moles) of 1,1-Bis(4-hydroxyphenyl)-1-(4-bromophenyl)-2,2,2,-trifluoro ethane and 4.73 grams (.01761 moles) of 2,1,5-diazo sulfonyl chloride and 2.03 grams (0.00765 moles) of 2,1,4-diazo sulfonyl chloride and 18 ml. of gamma- Butyrolactone (BLO) and 10 ml of acetone. The mixture was stirred at room temperature (25°C) for about 30 minutes to obtain a clear solution.

A separate solution of 4.52 grams (.0403 moles) of 1,4 - diazobicyclo (2.2.2) octane in 17 ml of BLO and 8 ml of acetone was added into the reaction flask by using a dropping funnel over a period of 10 minutes while maintaining the temperature at 30°C. The reaction mixture was stirred for 1 hour at room temperature. After the reaction was complete, 2 ml. of glacial acetic acid was added to destroy any unreacted sulfonyl chloride. The reaction mixture was stirred for one hour and then filtered to remove salt and any impurities.

- 11 -

The reaction mixture was precipitated by drowning into a mixture of 220 ml. deionized water and 20 ml. of methanol. A yellow fine precipitate was obtained, which was stirred for several hours then decanted, filtered and washed with about 3 liters of deionized water. The yellow cake was air dried first at room temperature by drawing
5 air through a buchner funnel. When the cake was air dried, it was placed in a vacuum oven at 35°C overnight. HPLC data indicated ester distribution to be: 2,1,4/2,1,5 (F/L) Bis Ester 47.25%; 2,1,5/2,1,5-(L/L) Bis Ester 22.02%; 2,1,4/2,1,4 (F/F) Bis Ester 27.11% and Unreacted 2,1,4-diazo Acid/Other Esters 2-4%.

EXAMPLE 2

10 Lithographic Evaluation of 2,1,4- and 2,1,4-Diazo Ester
of 1,1-Bis(4-hydroxyphenyl)-1-(4-bromophenyl)-2,2,2,-trifluoro ethane
(from Example 1):

A formulation of 1,1-Bis(4-hydroxyphenyl)-1-(4-bromophenyl)-2,2,2,-trifluoro ethane diazo ester (PAC) was prepared by mixing with a 26% solution of a m-
15 cresol/3,5-xyleneol (5:3 ratio) Novolak resin (NR) in PGMEA. The formulations were spin coated on silicon wafers at about 4000 RPM to obtain 1-1.2 micron film thickness. The wafers were soft baked in an air oven at 90°C for 30 minutes. All wafers were developed using 0.263n TMAH developer at 25+/-0.5°C. The following parameters were evaluated:

20

<u>Example</u>	<u>%</u> <u>PAC</u>	<u>RO</u>	<u>R</u>	<u>R/RO</u>	<u>Photospeed</u> <u>(mj/cm²)</u>
#2	12.0	12	44256	3688	130

RO = Dark Film Loss

R = Dissolution Rate of Fully Bleached Film

PAC = 2,1,4-Diazo Ester of Phenolphthalein

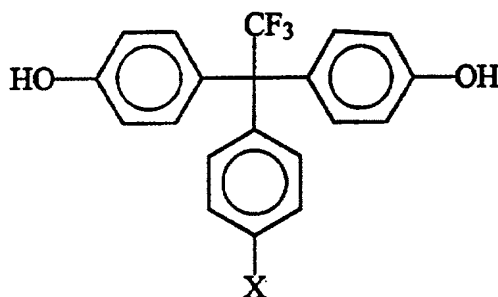
- 12 -

High R/O values indicate greatest differential between exposed and unexposed film loss which affects photospeed and contrast. In comparison to conventional Diazo esters R/O values are higher for phenolphthalein Diazo esters.

- 5 **RESOLUTION:** Using the formulation of Example 2, 0.5 micron line and space patterns were printed. The dose required to print 0.5 micron geometry using 1.0 micron thick film was about 170 mj/cm². The wall profile was nearly vertical and there was no scum at the surface of the film.

What is claimed is:

1. A positive photoresist composition comprises an admixture of:
 - (a) a photosensitizer comprising a diazo ester having the following structure:



X = Cl, Br, I, OH, OR, COOR, COOAr(OH)_n, COAr(OH)_n, COR, R, Ar(OH)_n

R = C₁-C₈ alkyl, n = 0 to 5, Ar = Phenyl

as the backbone, where the diazo ester is a compound wherein at least one hydroxy group on the phenyl ring has been esterified with a diazo sulfonyl chloride comprising 60 to 100 mole % 2,1,4 or 2,1,5 diazosulfonyl chloride, or a mixture thereof; the photosensitizer being present in the photoresist composition in an amount sufficient to uniformly photosensitize the photoresist composition; and

- (b) a water insoluble, aqueous alkali soluble novolak resin, the novolak resin being present in the photoresist composition in an amount sufficient to form a substantially uniform photoresist composition.

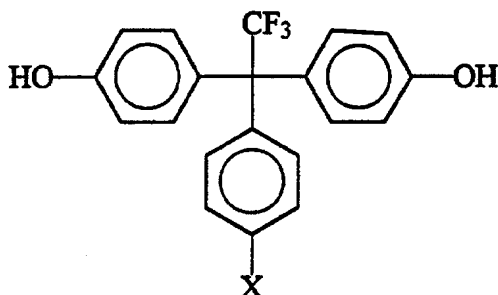
2. The composition of claim 1 further comprising one or more solvents.
3. The composition of claim 2 wherein said solvent comprises propylene glycol monomethyl ether acetate.

- 14 -

4. The composition of claim 1 wherein (a) is present in an amount of from about 1 to about 35 weight percent and (b) is present in an amount from about 65 to about 95 weight percent, based on the non-solvent components of the composition.
5. The composition of claim 1 wherein said solvent comprises ethyl-3-ethoxypropionate.
6. The composition of claim 1 further comprising one or more additives selected from the group consisting of colorants, leveling agents, anti-striation agents, plasticizers, adhesion promoters, speed enhancers and surfactants.
7. A photosensitive element comprising a substrate and the dried composition of claim 1 coated on said substrate.
8. The element of claim 7 wherein the substrate is selected from the group consisting of silicon, aluminum, polymeric resins, silicon dioxide doped silicon dioxide, gallium arsenide, Group III/V compounds, silicon nitride, tantalum, copper, polysilicon, ceramics and aluminum/copper mixtures.
9. The element of claim 7 wherein the substrate has an adhesion promoted surface.
10. The element of claim 7 wherein the composition further comprises one or more components selected from the group consisting of non-aromatic colorants, dyes, anti-striation agents, leveling agents, plasticizers, adhesion promoters, speed enhancers and surfactants.
11. The element of claim 7 wherein (a) is present in an amount of from about 1 to 35 weight percent and (b) is present in an amount of from about 65 to 99 weight percent, based on the non-solvent components of the composition.

12. A method for producing a photoresist image on a substrate, which comprises coating a substrate with a positive working photosensitive composition which composition comprises in admixture:

- (a) a photosensitive component comprising a diazo ester having the following structure:



X = Cl, Br, I, OH, OR, COOR, COOAr(OH)_n, COAr(OH)_n, COR, R, Ar(OH)_n

R = C₁-C₈ alkyl, n = 0 to 5, Ar = Phenyl

as the backbone, where the diazo ester is a compound containing at least one hydroxy group on the phenyl ring which has been esterified with a diazo sulfonyl chloride comprising 60 to 100 mole % 2,1,4 or 2,1,5 diazo sulfonyl chloride or a mixture thereof, said photosensitive component being present in the photoresist composition in an amount sufficient to uniformly photosensitize the photoresist composition; and

(b) a water insoluble, aqueous alkali soluble novolak resin; said novolak resin being present in the photoresist composition in an amount sufficient to form a substantially uniform photoresist composition and a solvent composition; and heat treating said coated substrate until substantially all of said solvent composition is removed; imagewise exposing said photosensitive composition to actinic radiation; and removing the imagewise exposed areas of said composition with an aqueous alkaline developer.

13. The method of claim 12 further comprising heating said coated substrate from a temperature of from about 90°C to about 150°C for from about 30 seconds to about 180 seconds on a hot plate or from about 15 minutes to about 40 minutes in an oven, after the exposure step but before the removing step.

14. The method of claim 12 further comprising heating said coated substrate at a temperature of from about 90°C to about 150°C for about 30 second to about 180 seconds on a hot plate or for from about 15 minutes to about 40 minutes in an oven, after the removing step.

15. The method of claim 12 wherein said substrate comprises one or more components selected from the group consisting of silicon, aluminum, polymeric resins, silicon dioxide, doped silicon dioxide, silicon nitride, tantalum, copper, polysilicon, ceramics, aluminum/copper mixtures, gallium arsenide and Group III/V compounds.

16. The method of claim 12 wherein the exposure step is conducted with actinic, x-ray or ion beam radiation.

17. The method of claim 12 wherein the exposure step is conducted with ultraviolet radiation having a wavelength of about 365 nm.

18. The method of claim 12 wherein the developing step is conducted with sodium hydroxide, potassium hydroxide or tetramethyl ammonium hydroxide.

19. The method of claim 12 wherein the composition further comprises one or more components selected from the group consisting of non-aromatic colorants, dyes, anti-striation agents, leveling agents, plasticizers, adhesion promoters, speed enhancers, and surfactants.

- 17 -

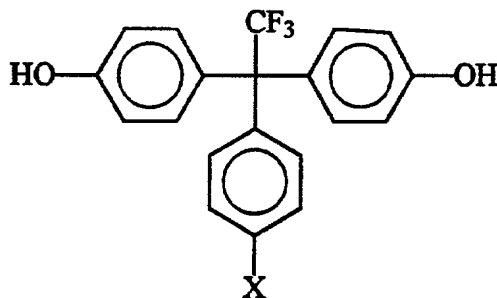
20. The method of claim 12 wherein (a) is present in an amount of from about 1 to about 35 weight percent and (b) is present in an amount of from about 65 to about 99 weight percent, based on the non-solvent parts of the composition.

21. The method of claim 12 wherein the solvent composition comprises one or more solvents.

22. The method of claim 12 wherein the solvent comprises propylene glycol monomethyl ether acetate.

23. The method of claim 12 wherein the solvent comprises ethyl-3-ethoxy propionate.

24. A photosensitizer comprising a diazo ester having the following structure:



X = Cl, Br, I, OH, OR, COOR, COOAr(OH)_n, COAr(OH)_n, COR, R, Ar(OH)_n

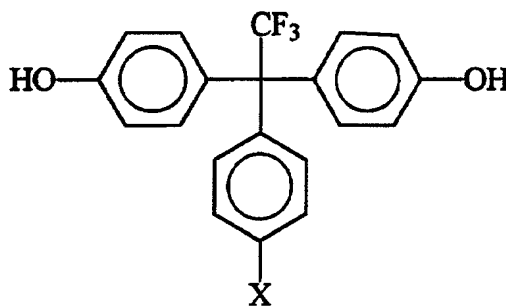
R = C₁-C₈ alkyl, n = 0 to 5, Ar = Phenyl

where the diazo ester is a compound wherein at least one hydroxy group on the phenyl ring has been esterified with diazo sulfonyl chloride comprising of 60 to 100 mole % 2,1,4- or 2,1,5- diazosulfonyl chloride, or a mixture thereof.

25. A method for producing a positive working photosensitive composition which comprises providing an admixture of:

- 18 -

- (a) a photosensitive component comprising a diazo ester having the following structure:



X = Cl, Br, I, OH, OR, COOR, COOAr(OH)_n, COAr(OH)_n, COR, R, Ar(OH)_n

R = C₁-C₈ alkyl, n = 0 to 5, Ar = Phenyl

- as the backbone, where the diazo ester is a compound containing at least one hydroxy group on the phenyl ring which has been esterified with a diazo sulfonyl chloride comprising 60 to 100 mole % 2,1,4 or 2,1,5 diazo sulfonyl chloride, or a mixture thereof, said photosensitive component being present in the photoresist composition in an amount sufficient to uniformly photosensitize the photoresist composition; and
- (b) a water insoluble, aqueous alkali soluble novolak resin; said novolak resin being present in the photoresist composition in an amount sufficient to form a substantially uniform photoresist composition and a solvent composition; and heat treating said coated substrate until substantially all of said solvent composition is removed; imagewise exposing said photosensitive composition to actinic radiation; and removing the imagewise exposed areas of said composition with an aqueous alkaline developer.

26. The method of claim 24 wherein the photoresist composition further comprises one or more components selected from the group consisting of non-aromatic colorants,

dyes, anti-striation agents, leveling agents, plasticizers, adhesion promoters, speed enhancers, and surfactants.

27. The method of claim 25 wherein (a) is present in an amount of from about 1 to about 35 weight percent and (b) is present in an amount of from about 65 to about 99 weight percent, based on the non-solvent parts of the composition.

28. The method of claim 25 wherein the solvent composition comprises one or more solvents.

29. The method of claim 25 wherein the solvent comprises propylene glycol monomethyl ether acetate.

30. The method of claim 25 wherein the solvent comprises ethyl-3-ethoxy propionate.

INTERNATIONAL SEARCH REPORT

International Application No
PC1/US 95/12719A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G03F7/022 G03F7/004

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 504 724 (SUMITOMO CHEMICAL CO) 23 September 1992 see the whole document ---	1-30
Y	EP,A,0 493 923 (HOECHST CELANESE CORP) 8 July 1992 see the whole document ---	1-30
Y	EP,A,0 430 477 (NIPPON ZEON CO) 5 June 1991 see the whole document ---	1-30
A	EP,A,0 468 531 (FUJI PHOTO FILM CO LTD) 29 January 1992 see the whole document -----	1-30

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

5 February 1996

Date of mailing of the international search report

19. 02. 96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Rasschaert, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCI/US 95/12719

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0504724	23-09-92	JP-A- 4284454	09-10-92
EP-A-0493923	08-07-92	US-A- 5260162	09-11-93
		JP-A- 6027663	04-02-94
EP-A-0430477	05-06-91	JP-A- 3158856	08-07-91
		US-A- 5306596	26-04-94
EP-A-0468531	29-01-92	DE-D- 69105848	26-01-95
		DE-T- 69105848	27-07-95
		JP-A- 4089469	23-03-92
		US-A- 5384227	24-01-95
		US-A- 5312905	17-05-94